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Studies of thermooxidative degradation process of chlorinated natural rubber from latex

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Abstract

The thermooxidative degradation of chlorinated natural rubber (CNR) from latex were studied by thermogravimetry (TG) coupled with Fourier Transform Infrared Spectroscopy (FTIR), ultraviolet-visible (UV-Vis) spectroscopy and difference FTIR. The CNR degraded in air atmosphere with two distinct steps of weight loss. The first step ranging from 160 to 390 °C, mainly is a dehydrochlorination reaction with a little oxidative scission of molecular backbones to release carbon dioxide and the conjugated polyene sequences $(\text{–[C=C]–})_{n=3,4}$ are formed on the molecules of CNR. The second step ranging from 390 to 585 °C, is an oxidative degradation reaction of the molecular backbones of CNR and the evolved gas is only carbon dioxide.

Keywords: Chlorinated natural rubber; Thermooxidative degradation; TG-FTIR coupling analysis; UV-Vis spectroscopy; Difference FTIR

1. Introduction

The chlorinated natural rubber (CNR) is a kind of white powder product prepared by the chlorinated modification of natural rubber (NR) from solution or latex. Because of the properties such as good filming formation, unique acid-proof, alkali-proof, corrosion-resistance, anti-penetrability, inflame-resistance and thermal stability, the CNR has been applied in the production of the raw materials for paints and adhesives, additive for ink, and acid-proof and alkali-proof products. In the typical solution process, the chlorination was carried out in the solution by dissolving natural rubber into CCl_4. Because the molecular chains of natural rubber are in unfolding states in the solution, the chlorination reaction of natural rubber can be proceeded more easily and the structures and properties of the product are more homogenized and unanimous accordingly [1–3]. Quite a lot of research workers studied the structures, properties and preparation reaction mechanism of CNR from solution in detail [4–12]. But the traditional CCl_4 solution process has been prohibited in many countries for it has the defects such as the high equipment investment, the serious problem of environmental pollution and the harmful to the health of workers. This makes the production of CNR from latex have a vast vistas. By controlling the chlorination reaction conditions properly and improving the stability of natural rubber latex with nonionic surfactant, the chlorination of natural rubber is available in latex directly [13–15]. Because the natural rubber exists in the form of colloid particles in latex, the chlorination reaction which concentrated mainly on the outer parts and then gradually into the inter parts of the rubber particles is difficult to proceed. The FTIR analyses of the structures of CNRs from solution and latex processes demonstrates that the main abnormal groups existing on the molecular chains of CNR from latex are carboxyl groups, whereas those on the molecular chains of CNR from solution mainly are hydroxyl groups [16]. This article reports the thermooxidative degradation of CNR from latex by use of the thermogravimetric analysis (TGA)/FTIR coupling system. The compositions of gases evolved during the thermooxidative degradation of CNR were identified and the in situ structure variations of CNR during degradation were also analyzed.

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2. Experimental

2.1. Materials and reagents

NR latex, high ammonia preserved concentrated natural rubber latex with a dried rubber content (DRC) of 60 wt.%, was obtained from Jianshe state-owned farm in Zhanjiang, PR China.

Octadecenyl alcohol-polyethylene oxide, chemically pure reagent, was obtained from Cook Co. Tetrahydrofuran (THF), analytically pure reagent, was obtained from Shanghai chemicals Co. PR China.

2.2. Preparation of CNR

One hundred grams NR latex (with DRC of 60 wt.%) was stabilized with octadecenyl alcohol-polyethylene oxide and then diluted to a DRC of 20 wt.%. 200 ml distilled water was added into a three-neck round-bottomed flask and the temperature was kept at 35 °C with a hot water bath. The chlorine gas was passed into the water to saturation and then the stabilized NR latex was added while sterring. In the same time the chlorine gas was passed into the flask continuously. The CNR with preliminary chlorination would be produced. Keep passing the chlorine gas into the flask for 24 h before the reaction was stopped. The product was neutralized to make the pH of the reaction system 7–8 with the sodium hydroxide solution (20%). The product was filtrated and washed with distilled water repeatedly, and then was dried under vacuum at 50 °C to get the powder CNR sample.

2.3. Determination of chlorine content

The chlorine content of the CNR determined according to Volhard method [17] is 65 wt.%.

2.4. TG/FTIR analysis

TG/FTIR analysis was performed on a Dupont-2100 thermal balance coupled with a Nicolet-550 FTIR spectrometer. The samples of 8.00 mg were scanned at 10 °C min^{-1} from 30 to 600 °C under air atmosphere with a flow rate of 50 ml min^{-1}. The evolved gases were passed through TG-FTIR coupling nozzle into the gas analysis cell with air. The TG and DTG curves were recorded ranging from 30 to 600 °C. In the same time, the evolved gases were scanned with FTIR continuously to get the Gram–Schmidt curve and the FTIR spectra of evolved gases of CNR. The FTIR spectra were recorded in the wave number range 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1}, and the scanning frequency is 20.

2.5. UV-Vis spectroscopy analysis

Ultraviolet-visible (UV-Vis) spectroscopy analysis was carried out on a Perkin-Elmer Lamda 2 UV-Vis spectrophotometer. The CNR samples of 1.0 g were heated at 160 °C in a hot air aging chamber for 5, 10, 20, 40, and 60 min, respectively. The degraded samples were dissolved in THF with the concentration of 1.0 mg/ml, and then scanned from 200 to 600 nm on an UV spectrophotometer. A reference cell loaded with the THF was used to eliminate any signals due to the solvent itself.

2.6. Difference FTIR analysis

The FTIR analysis was carried out on a Nicolet 550 FTIR spectrometer. The CNR sample was pressed into disc with KBr and put into a special designed aging vessel. The vessel consisted of cylindrical quarts tube (200 mm long, 20 mm in diameter) which was placed within the optical path of infrared spectrometer. The entire assembly could be insulated with graphite. Degradation experiment was performed by heating the sample disc with the annuloid resistance heater which was controlled to within 1 °C by a temperature programming-controller. The sample was degraded at a heating rate of 20 °C min^{-1} from ambient temperature to 360 °C. The gases released during the degradation of CNR was removed by air flow. Progressive spectral changes as a result of thermooxidative degradation can be obtained by subtraction of the IR spectrum of un-degraded CNR from the IR spectra of CNR degraded at 80, 250, 300 and 360 °C, respectively, to give the difference spectra as shown below:

$$\begin{aligned}\text{difference spectrum} = {} & k_\mathrm{d}(\text{spectrum of degraded CNR}) \\ & - k_\mathrm{u}(\text{spectrum of un-degraded CNR})\end{aligned}$$

where k_d and k_u are variables which can be used to compensate for differences in sample disc thickness. In this study, $k_\mathrm{d}/k_\mathrm{u}$ is 1 because identical area of the same sample was scanned each time. Any increase in absorbance above the base line is a result of an increment of new species whereas any decrease in absorption below the base line indicates a decrement of existing species. The FTIR difference spectra were recorded in the wave number range 4000–400 cm^{-1} with a spectral resolution of 4 cm^{-1}, and the scanning frequency is 20.

3. Results and discussion

3.1. TG analysis of CNR

Fig. 1 depicts the TG and DTG curves of thermooxidative degradation of CNR in air. The CNR degrades in air atmosphere with two distinct steps of weight loss leaving about 0.3 wt.% of residue at 585 °C. The first weight loss peak ranges from 160 to 390 °C, and the weight loss is about 69 wt.%. The second weight loss peak ranges from 390 to 585 °C and the weight loss is 31 wt.%.

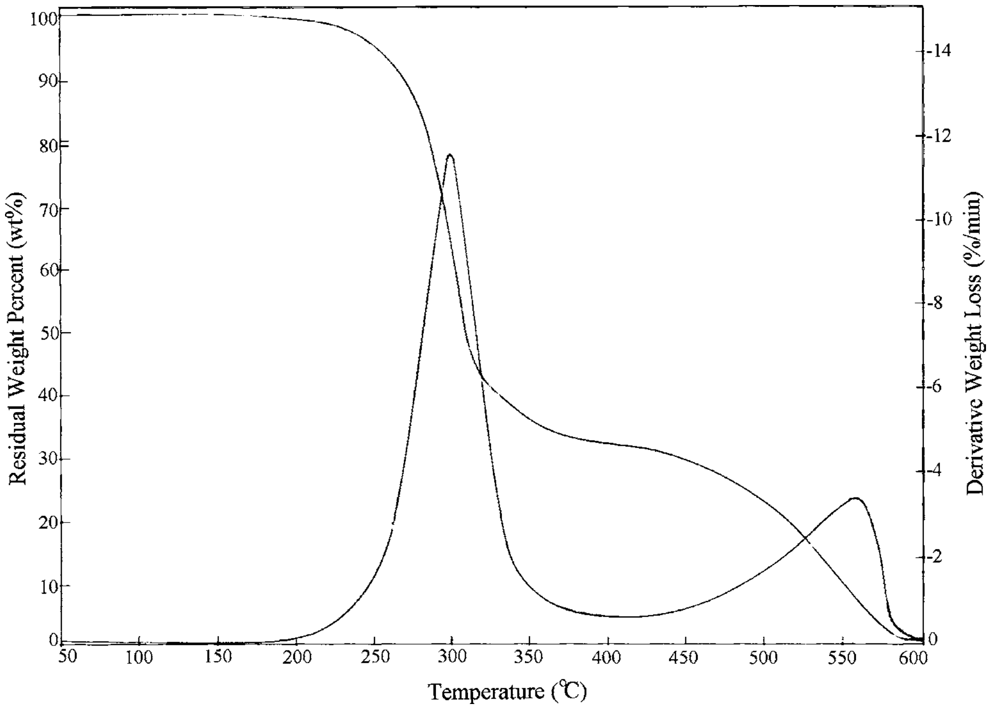

Fig. 1. TG and DTG curves of thermooxidative degradation of CNR in air.

3.2. *Identification of evolved gases during thermooxidative degradation of CNR*

The Gram–Schmidt curve of the evolved gases during the thermooxidative degradation can be obtained by Gram–Schmidt vector orthogonalization method (see Fig. 2). There are two distinct peaks on the Gram–Schmidt curves. The peak at 23.27–28.31 min on the Gram–Schmidt curve corresponds to the gases evolved in the first step reaction. The peak at 41.54–46.43 min corresponds to the gases evolved in the second step reaction.

Fig. 3 depicts the IR spectra of the evolved gas at 23.27–28.31 min in the first step of thermooxidative degradation of CNR, which shows the typical absorbance peaks at 3100 and 2600 cm^{-1}, as well as a weak absorbance at 2380 cm^{-1}. By comparing with the standard spectra, the gases evolved during the first step of thermooxidative degradation of CNR mainly are HCl with a little amount of CO_2, indicating that HCl is eliminated from the molecular chains of CNR by the scission of C–Cl and C–H bonds at 160–390 °C. In the same time, a little oxidative reaction occurs on the backbones of CNR.

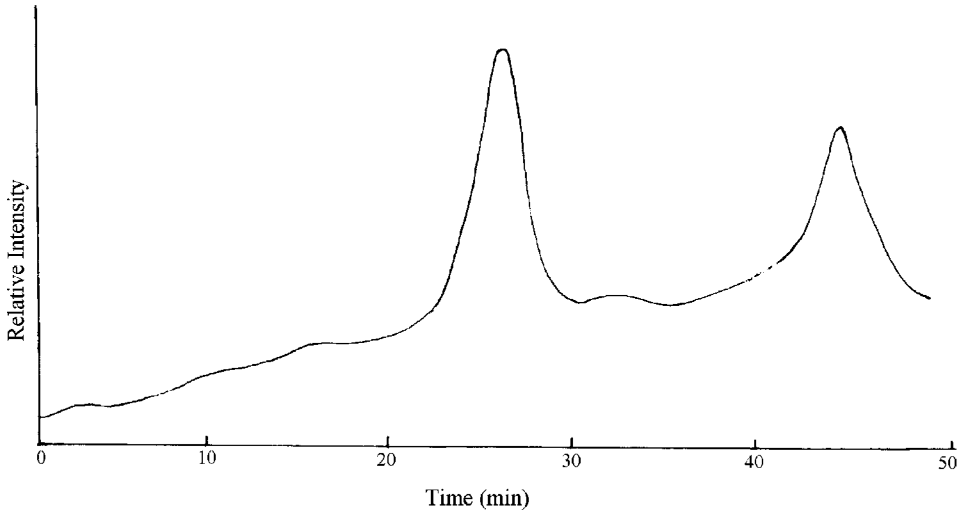

Fig. 2. Gram–Schmidt curve for thermooxidative degradation of CNR in air.

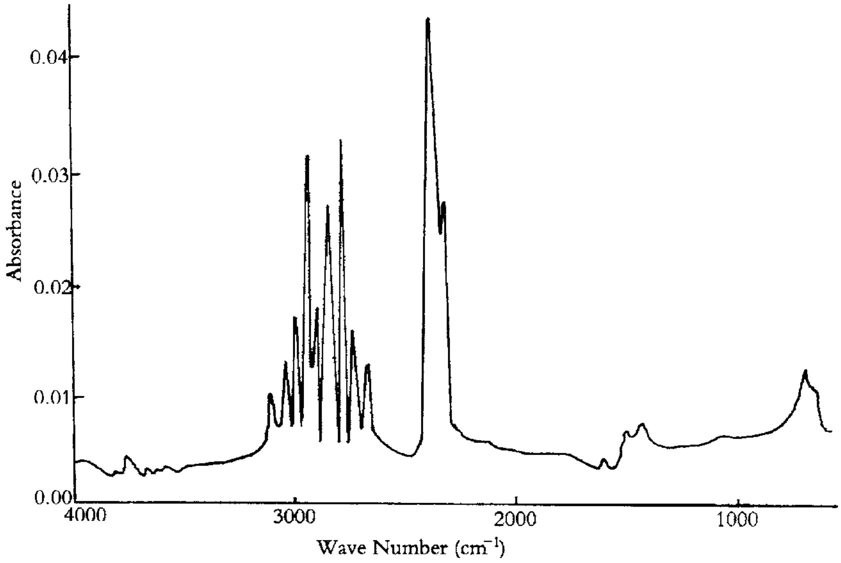

Fig. 3. IR spectra of gases evolved during the first step of thermooxidative degradation of CNR in air.

Fig. 4 shows the IR spectra of the evolved gases at 41.54–46.43 min in the second step of the thermooxidative degradation of CNR. A strong absorbance peak appears at 2380 cm^{-1}, indicating that the corresponding product is only CO_2, which is produced by the oxidative scissions of backbones of CNR.

3.3. UV-Vis spectroscopy analysis of in situ structure of the degraded CNR

Fig. 5 shows the UV-Vis spectra of CNR degraded in air at 160 °C for different times. A main absorb peak appears at around 245 nm on each spectrum, which might be assigned to the π–π* transition of conjugated polyene $-[C{=}C]_3-$ [18]. With the prolongation of degrading time, a peak at about 290 nm appears gradually. This peak might be assigned to the π–π* transition of conjugated polyene $-[C{=}C]_4-$ [18]. Because this peak is very wide, it is reasonable to presume that some other species which can not be identified the time being are produced as well. From Fig. 5 it can be seen that the intensities of the absorbances of both the peaks increased along with the prolonging of degradation time.

This is different from the thermooxidative degradation of PVC in air. During the thermooxodative degradation of PVC, the conjugated polyene sequences $(-[C{=}C]-)_n$ with the n ranging from 3 to 15 were produced from the elimination of HCl [18]. The possible reason is that the main backbone structures of PVC are of straight chains and the HCl can be easily eliminated through a “zipper” dehydrochlorination reaction [18], whereas those of CNR from latex are of cycle

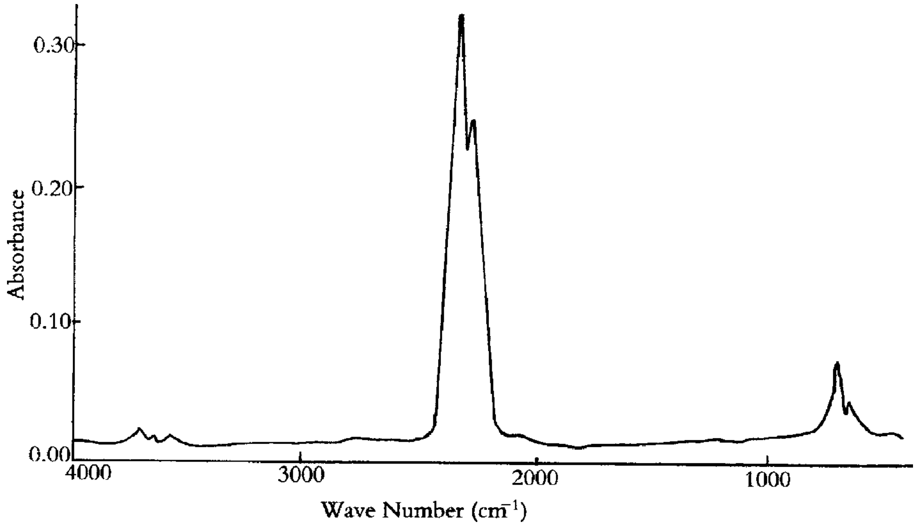

Fig. 4. IR spectrum of gas evolved during the second step of thermooxidative degradation of CNR in air.

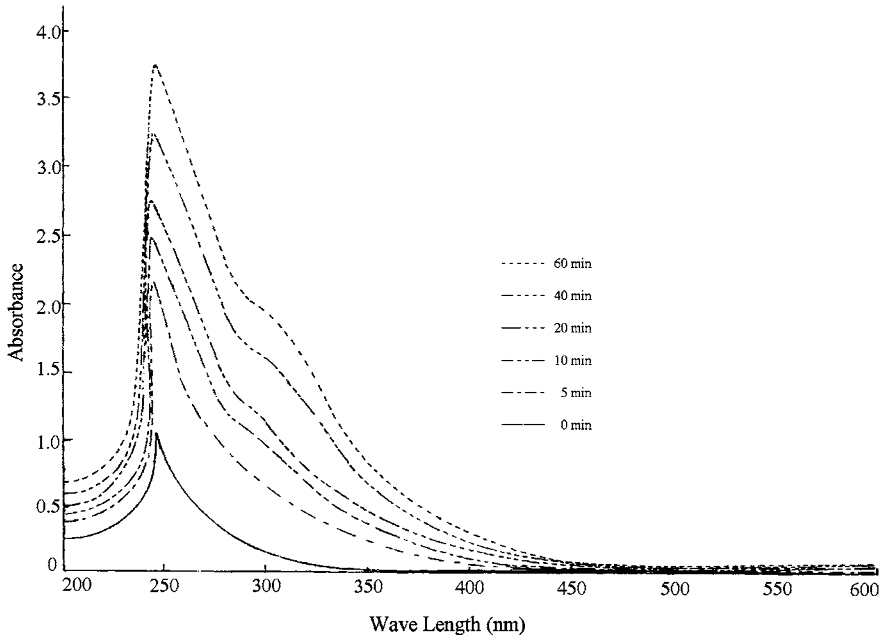

Fig. 5. UV-Vis spectra of CNR degraded at 160 °C in air for different times.

and crosslinking structures [12] and the dehydrochlorination reaction might be retarded somehow.

3.4. Difference FTIR analyses of thermooxidative degradation of CNR

In order to facilitate the analysis for the thermooxidative degradation of CNR in air, changes in the chemical structures of CNR are presented in the form of difference spectra as shown in Fig. 6.

With the release of HCl, a reduction in C–Cl bonds is observed as shown by the decrease in the absorption bands at 670 cm^{-1}. The further rising of the temperature makes the stretching absorbance of C–Cl at 730 and 790 cm^{-1} [6–9] begin to decrease and become more and more obvious, indicating that the C–Cl bonds on CNR molecular chain are not stable. The absorbances at 2975 and 970 cm^{-1} are attributed to the stretching and bending vibrations of C–H of methylene. The C–H absorbance of methylene with adjacent chlorine atom (–CH_2–(–CHCl)–) appears at 1430 cm^{-1} [6–9,16]. The intensities of these absorbances as well as that of the absorbance of C–H in –CHCl– at 1275 cm^{-1} decreased with the increase of degradation temperature. At the same time, the intensities of absorbance at 1587 cm^{-1} which is assigned to the stretching vibration of C=C of conjugated polyene sequences [19] increased gradually with the temperature rising. The decrements of the absorbances at 3450 and 1740 cm^{-1} mean the elimination of carboxylic groups from CNR molecular chains. These results further confirm that, during the degradation of CNR, HCl is eliminated from CNR molecular chains and the conjugated polyene sequences are formed before the backbones of CNR are oxidized into CO_2.

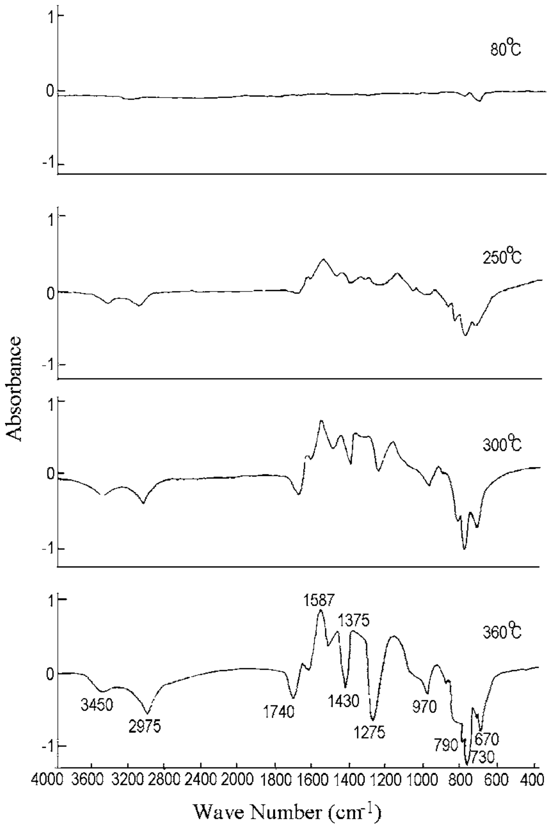

Fig. 6. IR difference spectra of CNR degraded at different temperatures in air.

4. Conclusions

The CNR from latex degraded in air with two distinct steps of weight loss. The first step ranges from 160 to 390 °C and the second one ranges from 390 to 585 °C. In the first step, the hydrogen chloride was eliminated from the molecules of CNR along with a little amount of carbon dioxide released and the conjugated polyene sequences $(–[C=C]–)_{n=3,4}$ were formed on the residual CNR molecules. In the second step, the backbones of CNR were oxidized into carbon dioxide with 0.3 wt.% residue remained.

Acknowledgements

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